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BY

JULIA LOOMIS MATTHEWS

A THESIS

Submitted to the Faculty
of
Michigan State College
In Partial Fulfillment of the
Requirements for the Degree
of
Doctor of Philosophy

Department of Chemistry
East Lansing, Michigan
1930

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The Activity Coefficient of 1 M HBr and the Single Electrode Potential of mercury, mercurous bromide in 1 molal HBr; and a new effect, due to adsorption, on the e. m. f. of the cell.

1. INTRODUCTION AND LITERATURE

The only previous work done on this identical cell was by R. H. Gerke and H. Geddes. (J. Phys. Chem. 31, 886-9 (1927). The studies were carried out with a single concentration at 25°C and the measurements were made by use of a glass cell with certain special features to prevent diffusion of the electrolyte from one-half cell to the other.

The present investigation was carried out in an attempt to obtain further evidence of the values of the above cell at several temperatures. It has been necessary to give careful study to the various factors effecting the e. m. f. An explanation is offered to account for certain effects which have heretofore appeared quite anomolous.

Up to the present time four workers have reported activity coefficients for HBr, based on e. m. f. measurements.

G. N. Lewis and Hyman Storch: (J. Am. Chem. Soc. 39, 2544 (1917) measured the potential of Br in KBr at 25° against the calomel electrode, and the potential of the same Br in HBr against the hydrogen electrode.

Bates and Kirschmann: (J. Am. Chem. Soc. 41, 1991 (1919) measured vapor pressures of HBr at 25°C and evaluated activity coefficient.

R. S. Livingston: (J. Am. Chem. Soc. 48, 45-53 (1926) measured the e. m. f. of cells of the type H, HBr (x m), AgBr, Ag having a concentration range of .08 to 1.55 M. He evaluated the activity of HBr in pure aqueous solution and solutions containing sulphates.

H. Harned (J. Am. Chem. Soc. 51, 416 (1929) evaluated activity coefficients of HBr during the study of electromotive forces of univalent halides in concentrated aqueous solutions. He studied various cell types, including the cell H_2, HBr, AgBr, Ag.

Harned, working with James (J. Phys. Chem. 30, 1060-72 (1926) while studying the dissociation of water in KBr and NaBr solutions, made measurements of various other types of cells. Among them was the cell H_2, HBr (m_o), NaBr (m_1), AgBr, Ag. From the E they calculated the activity of the acid.

Other cells using the H_2, HBr electrode have been run under varying conditions. The chain (Pt), H_2, HBr (0.1N) + neutral Salt, KCl 1.0 N. 1.75 N, 3.5 N, KCl, 1.0 N, HgCl, Hg was studied by V. A. Arkadiev (J. Russ. Phys. Chem. Soc. 56, 96-106 (1924). This was done primarily to learn the effect of neutral salts upon the hydrogen electrode potential.

Bodenstein and Geiger (Z. physik Chem. 49, 70 (1904) studied the dissociation of HBr and HCl. They measured the cell + Pt, 1/2 Br_2 (c), HBr (c_2), H.

McIntosh (J. Phys. Chem. 2, 273 (1898) used cells of the type H_2, HBr (c_1), HBr (c_2), H_2 +. These concentration cells were studied with and without diffusion in order to determine the transference number of hydrogen.

A number of cells with Ag, AgBr electrodes have been measured to study various properties of solutions.
Zengelis (Z. physik. Chem. 12, 298 (1893): Goodwin, ibid., 12, 577 (1894); Loven, ibid., 20, 456 (1896); Luther, ibid, 30, 628 (1899); 36, 385 (1901); Kuster and Thiel (Z. Anorg. Allgem. Chem. 23, 25 (1900); Abegg and Cox (Z. physik. Chem. 46, 1 (1903); M. De K. Thompson (J. Am. Chem. Soc. 28, 731 (1906); J. N. Pearce and Hart, ibid., 43, 2483 (1921) measured e. m. f. of cells to determine the free energy of dilution and activities of ions of KBr in aqueous solutions; I. M. Kolthoff (Z anorg. allgem. Chem. 132, 117-24 (1923); C. Drucker and Schingnitz (Z. physik. Chem. 122, 149 (1926); Harned and Douglass (J. Am. Chem. Soc. 48, 3095 (1926) c. f. (J. Chem. Soc. 115, 1020 (1919); Gelbach and Huppke (J. Am. Chem. Soc. 48, 1504 (1926); Vanselow and Sheppard (J. Phys. Chem. 33, 331 (1929).

Some work has been done with use of mercurous bromide electrode in rather complex cells. Behrend (Z. physik. Chem. 11, 466 (1893); ibid 15, 498 (1894) found the e. m. f. of the cell, Hg, HgBr, N/10 KBr, N/10 KCl, HgCl, Hg.

Goodwin (Z. physik. Chem. 13, 577, (1894) measured the same cell at 17° C. E. = .1338 V.; also (Phys. Review 4, 242 (1897) measured cells of the type ZnHg, ZnBr (C_1), HgBr, Hg, HgBr, ZnBr (C_2), Zn + Hg and the same cell with AgBr, Ag, AgBr bridge.

Immerwahr (Z. Elecktrochem. 7, 477 (1900) measured Hg, HgBr, N/1 KNO_3 N/20 KBr, N. E.

Nernst (Z. physik. Chem. 4, 129 (1889) studied the following cells: E_{18} = .0417; Hg, HgBr, NaBr (0.125c), NaBr (0.0125c), HgBr, Hg+ E_{18} = .0932; Hg, HgBr, HBr (0.126c), HBr (0.0132)c, HgBr, Hg+.

Drucker (Z. Elecktrochem. 18, 562 (1912) measured +Hg, HgBr, KBr (c_1), KBr (c_2), HgBr, Hg. He also measured a similar cell; +Hg, HgBr, $BaBr_2$ (c_1), $BaBr_2$ (c_2), HgBr, Hg (Z. Elecktrochem. 19, 797 (1913).

Öholm (Acta Societatis feumcae 41, 3 (1912) measured HgCd 12.5%, $CdBr_2$ (Sat'd), Hg_2Br_2 paste, Hg and HgCd 12.5%, $CdBr_2$ Soln., Hg_2Br_2 paste, Hg.

A. E. Brodskii (Z. Elecktrochem. 32, 1 (1926) while evaluating the solubility products of Hg halides in water, measured the e. m. f. of the cell.

Hg, $Hg_2(NO_3)_2$ CO, K_{xc} Hg_2Br_2, Hg.

Measuring the cell:
Hg, $HgCl_2$ KCl (0.1), KBr (0.1) Hg_2Br_2, Hg he found E = .1282 and .1268 (Z. Elecktrochem. 32, 1-14 (1926). He refers to the values reported by Bugarsky (Z. anorg. allgem. Chem. 14, 145 (1897) for the same cell, E = .1280 and .1274 V.

Brodskii, (Z. Elecktrochem. 32, 5 (1926) reported values for the cells: +Hg, Hg_2Br_2 KBr (C_1), KBr (C_2) Hg_2Br_2, Hg⁻ in absolute methyl alcohol, and +Hg, Hg_2Cl_2 KCl (C_1), KBr (C_2), Hg_2Br_2, Hg in water.

Brodskii and Shershever (Ukrainskii Khem. Zhurnal 2, 289 (1926) measured the e. m. f. of the cell Hg, $Hg_2(NO_3)_2$, Hg, Hg_2Br_2, KBr at 11°C and 27°C in order to determine solubility products.

Getman (J. Phys. Chem. 32, 91 (1928) measured the cell Cd, $CdBr_2$(m), HgBr, Hg^+ and evaluated activity coefficients of $CdBr_2$ solutions.

Goodwin (Z. physik. Chem. 13, 653 (1894) Hg, Hg_2Br_2 1/100 N KBr, N KNO_3, 1/100 N KCl Hg_2Cl_2, Hg at 43.3°C E = .2149
18.0° E = .1285
0° E = .1311

II. PREPARATION OF SUBSTANCES

1. Mercury

All the mercury used in the cells or in preparation of substances was Merck's Analyzed product. This was run through small capillary tubes, and then electrolyzed by making it the anode in a 2% solution of nitric acid. The method was recommended by Wolff and Waters (Bull. Bur. Standards 3, 625 (1907). Electrolysis was continued for more than thirty hours. The Hg, now freed from metal impurities, was then washed and distilled in an all Pyrex apparatus at a pressure of 30 mm. in a current of air. If the Hg thus prepared did not have a mirror surface, it was redistilled before using. The product was kept free from moisture in a desiccator over calcium chloride.

2. Hydrobromic Acid.

Hydrobromic acid, as well as mercurous bromide, was not allowed to come into contact with white light. The laboratories, in which this work was carried out, were lighted only by means of Eastman Kodak Safe Lamps, provided with Wratten Safelights, Series 0, for use with Br papers.

All the acid used in the cells was prepared from Baker's Analyzed 34% HBr of specific gravity 1.3. This was fractionated in an atmosphere of nitrogen in an all Pyrex glass apparatus. The fourth fraction, retained as the constant boiling one, was then redistilled twice in an atmosphere of nitrogen just before dilutions were made.

The various molal solutions were made up by weight from conductivity water that had been evacuated. All necessary precautions were taken to prevent the acid solution from coming in contact with air. The Solutions were analyzed by precipitating with silver nitrate and weighing the silver bromide.

3. Mercurous Bromide.

Various methods were used in the preparation of mercurous bromide. In preliminary work the salt was made chemically by precipitating the bromide from the hydrobromic acid solution with mercurous nitrate. All the water used was first evacuated and the different methods carried out in either a nitrogen or a hydrogen atmosphere.

Two methods were used for preparing the salt electrolytically. The procedure was similar to that used by Ellis in making calomel (J. Am. Chem. Soc. 38, 740 (1916). Pure mercury was placed in a crystallizing dish and covered with a saturated solution of potassium bromide. The mercury was made the anode by means of a platinum wire and the cathode was a small vessel containing Hg, placed inside the larger dish and completely covered with the same potassium

bromide solution. Contact was made with another platinum electrode. The contents of the crystallizing dish were stirred constantly during electrolysis.

The mercurous bromide was also formed electrolytically in the presence of IN HBr. The salt formed by these methods did not give as reproducible results as that formed chemically.

The best mercurous bromide was prepared from recrystallized potassium bromide and mercurous nitrate. The mercurous nitrate was dissolved in water, filtered and added to the bromide solution, drop by drop, while the solution was being agitated, always keeping the potassium bromide in excess. At first rather concentrated solutions were used but later very dilute solutions seemed to be better on account of the great adsorption of the nitrate ion.

The precipitate was washed with about eight liters of water to insure a pure product. Tests were made on samples at intervals for presence of nitrate or potassium ions, but they were always negative. This washed bromide could be kept under water until ready for use.

The mercurous bromide to be used in cells, was filtered on a Buchner funnel as free of water as possible and transferred to a 500 cc separatory funnel filled with nitrogen. The precipitate was thoroughly washed with acid of the desired concentration. From the time that the precipitate was treated with acid until used in the cell all precautions were taken to exclude oxygen.

From this point, the procedure varied according to the series of cells to be run. For example in the two series, cells 65 - 68 and cells 69 - 72, the mercurous bromide in acid solution was divided into two parts, purified Hg added, and shaken mechanically for 48 hours. The solution appeared cloudy, so the acid was filtered off and a fresh dilution made. This was again shaken for 48 hours and the cells filled.

Two series, cells 77 - 84 and cells 86 - 93, were run to study the effect of length of shaking on the e. m. f. which will be described later in detail. In both cases, the acid bromide solution was carefully divided between four 250 cc separatory funnels, purified mercury added and shaken varying lengths of time.

Cells No. II_{1-8} and cells No. III_{1-6} were treated in a similar manner but each shaken for 60 minutes mechanically at a speed greater than previous cases.

The mercury was broken up into fine globules coated with the particles of mercurous bromide. This gave the appearance of a fine grayish black precipitate, the state of division depending upon the length of shaking.

4. Potassium Bromide.

For all experiments Baker's C. P. Analyzed KBr was used. The analysis showed the presence of .0346% K_2CO_3, .0025% bromates, 0.1% iodides, 0.01% sulphates, 0.002% Ba, and 1.5% KCl. The product was carefully purified by five recrystallizations, the final crystallization being made in a platinum dish.

5. Hydrogen.

Tank hydrogen was used for the experiments. The gas was purified by passing it through a specially built train, consisting of two 18 inch Pyrex tubes containing glass beads. The first tube containing pyrogallate solution (made by dissolving 160 grams KOH in 130 grams H_2O and adding to it 10 grains of pyrogallic acid) was connected to the second through a safety bottle. The second tube contained hydrobromic acid of the same concentration of the cell to be measured. This train was connected to a six foot coil of glass tubing, immersed in the oil bath, so that the hydrogen gas admitted to the hydrogen electrode vessel would be of the same temperature as the cell.

6. Nitrogen.

The nitrogen used was tank nitrogen from which the oxygen was removed by passing through a column of pyrogallate solution.

III. THE CELL: SETTING UP AND MEASUREMENTS.

The hydrogen electrode vessel was one of a simple type, consisting of a $4\frac{3}{4}$ inch cylinder, $1\frac{1}{2}$ inches in diameter and a tight fitting, sulphur free rubber stopper used to support the necessary tubes. See diagram (1.).

The siphon tube joining the hydrogen electrode vessel with the intermediate vessel consisted of about $3\frac{1}{2}$ feet of small tubing bent in 6 inch lengths. The stop cock placed on one arm served to prevent diffusion.

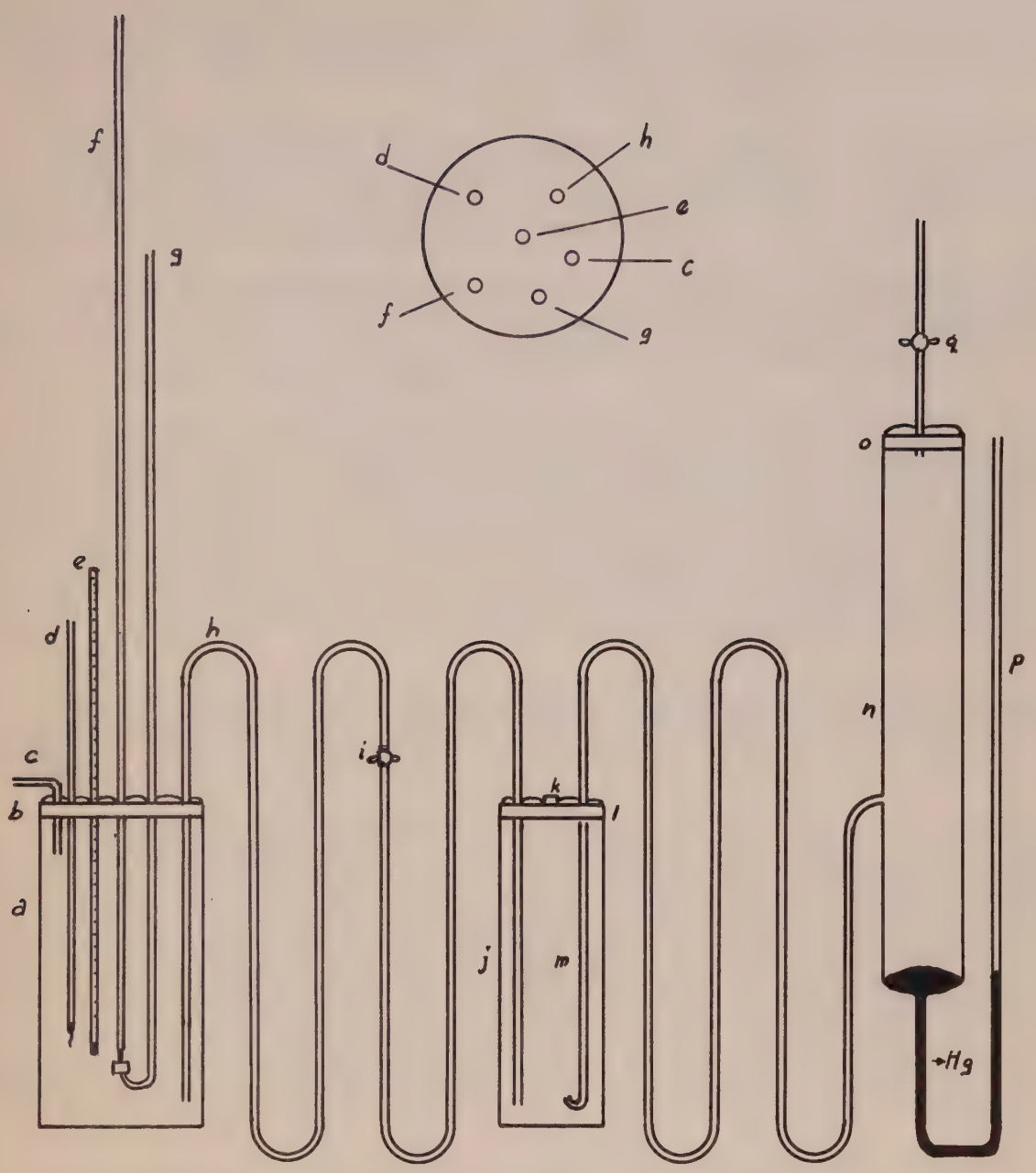
The platinum electrode was thoroughly cleaned by burning in the oxidizing flame of a Bunsen burner and then in an alcohol flame. The foil was platinized by making it the anode in a solution of pure chloroplatinic acid containing more than 1% platinum and a trace of lead acetate. A current sufficient to liberate gas freely at both electrodes was passed for fifteen or twenty minutes. The electrode was then washed carefully many times with conductivity water and allowed to soak at least 48 hours in order to remove all platinizing solution from the platinum black coating.

When the cell was ready to be assembled, the hydrogen electrode vessel and siphon were washed with hydrobromic acid of the desired molality and filled in an atmosphere of nitrogen.

The mercurous bromide electrode was also of a simple type constructed from a large Pyrex glass test tube. It was designed chiefly to prevent diffusion of the mercurous ion into the hydrogen half cell. See diagram (1.). The side arm of the cell consisted of $2\frac{1}{2}$ feet of small glass tubing, the end of which was constricted and bent upward.

The diameter of the tube was an inch, giving a fairly large mercury surface. In preliminary work, various types of cells were constructed and tried out for reproducible results. It was found that the best results were obtained by use of the described cell, where the surface was not too small nor too large.

Diagram (1)



a - H electrode vessel
b - S free rubber stopper
c - H outlet
d - auxilliary H-electrode
e - thermometer
f - H-electrode
g - H inlet
h - siphon tube.
i - stop cock
j - intermediate vessel
k - cork stopper
l - S free rubber stopper
m - side arm of HgBr electrode
n - HgBr electrode
o - No. 4 rubber stopper
p - tube for making Hg contact
q - stop cock

The two separate helf cells were first cleaned thoroughly and dried. After the H-electrode had been platinized and soaked, (a) and (h) (See diagram) were washed with the HBr to be used. (a) was filled 3/4 full of the acid, (b) inserted and (h) filled by means of nitrogen pressure.

The mercurous bromide electrode, (n) was now joined to the other half of the cell by inserting (m) through a slit in (l) which was then put firmly into the intermediate vessel (j). (o.) was put into place with (q) open and the mercurous bromide half cell was ready to fill.

Purified mercury was run into the arm (p) until it reached approximately a one half inch level in (n.).(k.) was removed and a stream of nitrogen gas filled the half cell and intermediate vessel with nitrogen through (q.). (k) was then replaced and (q.) closed.

The separatory funnel containing the mercurous bromide solution was then prepared. The stem was filled with nitrogen, and put down to the mercury level in (n.). By means of nitrogen pressure, about an inch of the heavy mercurous bromide paste was forced through the stem into (n.) which was again filled with nitrogen and (o) inserted and sealed with collodion. (k.) was removed and the saturated mercurous bromide solution run into (j.) until almost full. This solution was then drawn up through (q) until (n) was completely filled.

The cell was then placed in an oil bath and hydrogen bubbled through (g) for thirty minutes. No measurements that are trustworthy can be made for about 24 hours.

The apparatus for measurement of the e. m. f. of cells 1 - 77 consisted of a Leeds and Northrup potentiometer Type K (instrument No. 147352). For the remainder of the work a Wolff potentiometer (instrument No. 7012) was used. This gave more certain readings for the fifth decimal and seemed more satisfactory in every way. An Eppley Standard Cell (No. 23887) was used, which had recently been calibrated at the Bureau of Standards and certified to have a value of 1.01878 volts at 26° C. A high sensitivity Galvanometer Type R (Leeds and Northrup) was in the circuit. All the measuring system rested on a large copper sheet which acted as an equipotential shield. All the thermometers used were compared to thermometer No. 29291, which had been calibrated at the Bureau of Standards.

After setting up the cell as described above, allowing it to come to temperature equilibrium and hydrogen equilibrium, the potentiometer current was adjusted by aid of the Standard Cell. Contacts were made, and the e. m. f. of the experimental cell measured. When measurements were made, various effects studied, and the constancy of the cell noted, it was emptied, cleaned and refilled.

IV. ELECTRODE POTENTIALS.

Three series of experiments were run on molal solutions in order to evaluate the electrode potential of Hg, Hg_2Br_2, HBr (1M).

Table I shows the experimental results.

TABLE I

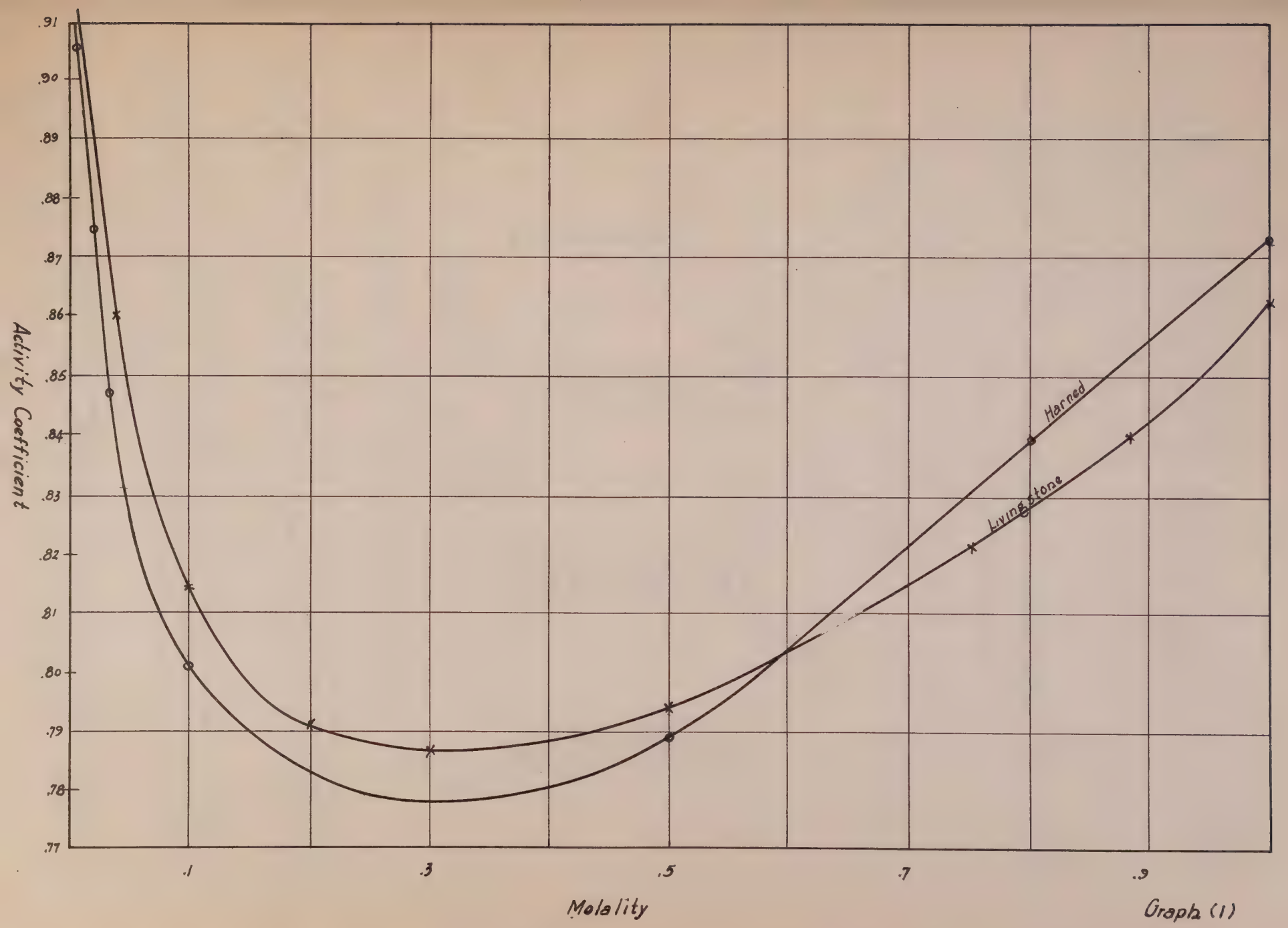
Cell No. l_1	Hrs.	E obs.	t obs.	Bar P. obs.	E corr. to 760 mm. 25° C.	HBr Conc.
	12.9	.15001	24.69	742.3	.15063	.9468
	42	.14970	24.70	737.2	.15041	
	60.6	.14972	24.68	727.9	.15059	
	89	.14978	24.70	737.6	.15048	
	115	.15016	24.70	743.4	.15076	
	132	.15010	24.72	748.1	.15062	
					.15058 = Av.	
Cell No. l_2	47.4	.14922	24.68	728.2	.15008	.9468
	64.4	.15001	24.70	737.6	.15071	
	85.4	.15002	24.72	743.4	.15062	
	111.4	.15004	24.74	748	.15057	
					.15049 = Av.	
Cell No. l_3	5.6	.14980	23.2	742.2	.15036	.9468
	17.1	.14967	23.2	743.3	.15021	
	45.5	.14975	21.4	748	.15018	
	67.5	.14961	25.1	751.2	.15011	
					.15021 = Av.	
Cell No. ll_1	23	.14743	25.05	728	.14830	.9745
	49	.14739	25.1	720.2	.14842	
	173	.14759	25.1	735.6	.14836	
	188.4	.14765	25.1	738.9	.14836	
	211.9	.14679	35.0	739.4	.14885	
	215.5	.14672	34.9	736.9	.14880	
	235.9	.14773	25	735.3	.14849	
	240.3	.14768	25	733.4	.14847	
					.14850 = Av.	
Cell No. ll_2	23	.14754	25.1	728	.14843	.9745
	46.6	.14742	25.1	720.7	.14844	
	171.6	.14755	25.1	735.6	.14832	
	188.1	.14755	25.1	738.9	.14826	
	212.5	.14665	34.92	739.4	.14868	
	217.5	.14656	34.9	736.9	.14864	
	237.2	.14756	25	735.3	.14832	
	241.6	.14748	25	733.3	.14827	
					.14842 = Av.	

Table I continued:

Cell No. 11_3	Hrs.	E obs.	t obs.	Bar P. obs.	E corr. to 760 mm. 25°C.	HBr Conc.
	22.5	.14759	25.1	727.1	.14850	.9745
	44.5	.14751	25.1	720.9	.14852	
	171.5	.14776	25.1	735.6	.14853	
	187.5	.14775	25.1	738.9	.14846	
	212.0	.14692	35	739.2	.14898	
	217.0	.14686	34.9	736.9	.14894	
	237.0	.14781	25	735.3	.14857	
	240.2	.14779	25	733.3	.14858	
					.14863 = Av.	
Cell No. 11_4	24	.14749	25.1	726.7	.14841	.9745
	43	.14752	25.1	720.4	.14854	
	169.4	.14762	25.1	735.6	.14839	
	188.7	.14763	25.1	739.4	.14833	
	212.7	.14664	34.92	739.2	.14868	
	216.7	.14654	34.9	736.9	.14862	
	237.3	.14732	25	735.3	.14808	
	239.7	.14715	25	733.4	.14794	
					.14837 = Av.	
Cell No. 11_5	17.7	.14724	25.2	728.8	.14812	.9745
	48	.14701	25.2	720.2	.14804	
	166.5	.14706	25.3	735.6	.14783	
	190.1	.14710	25.4	737.8	.14785	
	211.1	.14738	21.4	739.2	.14796	
	216.1	.14736	21.2	736.9	.14798	
	235.1	.14711	25.1	735.3	.14788	
	240.1	.14709	25	733.3	.14788	
					.14794 = Av.	
Cell No. 11_6	22	.14728	25.1	726.7	.14820	.9745
	42.5	.14723	25.1	720.6	.14825	
	168.7	.14739	25.1	735.6	.14816	
	187.1	.14711	25.1	739.4	.14781	
					.14810 = Av.	
Cell No. 11_7	17	.14719	25.2	729	.14807	
	46	.14711	25.1	720.2	.14814	
	165.7	.14729	25.4	735.6	.14807	
	187.2	.14735	25.4	739.1	.14807	
	208.7	.14749	21.4	739.4	.14807	
	215	.14741	21.2	739.6	.14803	
	232.5	.14713	25	735.3	.14789	
	238.5	.14708	25	733.3	.14787	
					.14802 = Av.	

Table I continued:

Cell No. 11_8	Hrs.	E obs.	t obs.	Bar P obs.	E corr to 760 mm 25°C.	HBr Conc.
	18	.14722	25.2	729	.14810	.9745
	45	.14707	25.2	720.2	.14810	
	166	.14727	25.4	735.6	.14805	
	186.7	.14734	25.4	739.1	.14806	
	208.1	.14754	21.4	739.4	.14812	
	214.1	.14749	21.2	736.9	.14811	
	231.5	.14711	25	735.3	.14787	
	237.5	.14724	25	733.3	.14803	
					.14805 = Av.	
Cell No. 111_1	20.5	.14483	25.5	745.2	.14545	1.0172
	43.5	.14480	25.1	748.6	.14534	
	68	.14466	25.05	741.1	.14533	
	90.7	.14455	25.01	739.2	.14524	
					.14534 = Av.	
Cell No. 111_2	21.5	.14477	25.1	744	.14539	
	43.5	.14481	25.05	748.9	.14535	
	66.7	.14466	25.05	741.1	.14533	
	91.0	.14454	25	738.8	.14524	
	239.0	.14423	25	728.3	.14511	
					.14528 = Av.	
Cell No. 111_3	21.9	.14482	25.1	743.9	.14544	
	44.9	.14481	25.05	748.3	.14537	
	68.3	.14457	25.05	739.7	.14526	
	92.8	.14443	25	738.5	.14513	
					.14518 = Av.	
Cell No. 111_4	22.4	.14477	25.1	743.1	.14541	
	43.9	.14486	25.05	748.3	.14542	
	67.4	.14468	25.05	739.7	.14538	
	91.9	.14460	25	738.5	.14530	
	238.9	.14423	25	728.3	.14511	
					.14532 = Av.	
Cell No. 111_5	18.5	.14517	25	744	.14578	1.0172
	40.5	.14524	25	748.6	.14577	
	65.0	.14510	24.9	741.1	.14576	
	87.6	.14498	25	739.2	.14567	
	237.6	.14437	25	728.3	.14525	
					.14564 = Av.	
Cell No. 111_6	17.5	.14518	25	745.2	.14577	1.0172
	41.5	.14529	25	748.9	.14582	
	66.2	.14522	25	739.7	.14590	
	86.6	.14496	25	739.2	.14565	
					.14578 = Av.	


.91
.90
.89
.88
.87
.86
.85
.84
.83
.82
.81
.80
.79
.78
.77
Activity Coefficient
.1
.3
.5
.7
.9
Molality
Harned
Livingstone

Graph (1)

By taking the mean value of the e. m. f. of the above series Cells No. 11_{1-8} and the value of Livingston for the activity of HBr in a 0.9745 M solution, Graph (1), it is shown that the value of the single electrode potential of Hg, Hg_2Br_2, HBr (1M) is - 0.13906 volt.

The calculation of this value was made from the familiar electrode equation:

$$E = \widetilde{E} - \frac{RT}{NF} \log \frac{c_1 \alpha_1}{c_2 \alpha_2}$$

where for 25° C. R T is 0.05913 and for concentration 0.9745 M becomes 0.858.

After making the proper substitutions there results:

$$E = \widetilde{E} - \frac{.05913}{2} \log (0.9745 \times 0.858)^4 \text{ and } \widetilde{E} = -0.13906 \text{ volt.}$$

If the value of Harned (α = 0.868) is used the E = - 0.13965 volt.

See Table II for results:

TABLE II

Cell No.	Average E corr. to 760 mm 25°C.	$\widetilde{E}$ Livingston α = 0.858	$\widetilde{E}$ Harned α = 0.868
11_1	.14850	.13931	.13990
11_2	.14842	.13923	.13982
11_3	.14863	.13944	.14003
11_4	.14837	.13918	.13977
11_5	.14794	.13875	.13934
11_6	.14810	.13891	.13950
11_7	.14802	.13883	.13942
11_8	.14805	.13886	.13945
		.13906 = Av.	.13965 = Av.

This value compares with that found by Gerke working with a single concentration (0.10015F) of - 0.139_6 volt.

(J. Phys. Chem. 31, 886-9 (1927). It is based upon the assumption that the activity coefficient of HBr in (0.10015F) HBr is 0.814.

In the I. C. T. Gerke reports the value of the single electrode potential as 0.1385 volt. If one calculates the value of α assuming the $\widetilde{E}$ is 0.1385V, the value of α is found to be 0.7927. Substituting Harned's α (0.802) for Livingston's α (0.814) and recalculating Gerke's results, one finds $\widetilde{E}$ = - 0.13901V.

In the work done by Gerke, some attention was given to guarding against the effects of light and the presence of oxygen. The presence of oxygen undoubtedly causes the e. m. f. to be increased and since this value of E compares very favorably to that of Gerke, it seems plausible that the absence of oxygen in the cells is assured.

Further criteria of the accuracy of these cells is noted in the unusual length of time they remained stable. The cells reported here remained stable for a period of 67 to 241 hours whereas those of Gerke were observed for 63 hours.

V. CORRECTION FOR BAROMETRIC PRESSURE.

The hydrogen electrode acts in a reversible manner and responds to either an increase or a decrease in hydrogen pressure. The corrections for the observed barometer readings were made on the basis that 1 cm. increase in pressure corresponds for small pressure changes to an increase of 0.00017 volt in e. m. f.

For corrections of the vapor pressure of water values 17.54 mm at 20° C. 23.76 mm at 25°C. and 42.17 mm at 35°C. were used. Corrections on the observed barometer reading were made in accordance with the weather bureau barometer.

VI. EFFECT OF TEMPERATURE AND CORRECTION FOR TEMPERATURE CHANGES.

For cells of concentration approximately 0.1 M, as the temperature increases there is an increase, in the e. m. f. of the cell. In order to obtain temperature coefficients for correcting the observed e. m. f., the cells were studied at three temperatures, 20°, 25° and 35°.

For coefficients for 0.1 M solutions, cells 86, 88, 89, and 90 were used. See the following Table:

TABLE III

Cell 86	Conc.	Hrs.	E obs.	t obs.	Bar P. obs.	E corr. to 760 mm 25°C.
	.09066	46.4	.27621	25.2	742.3	.27685
		64.4	.27580	25.1	737.2	.27657
		83.4	.27559	24.9	727.5	.27661
		98.9	.27597	25.1	737.6	.27673
		116.9	.27605	25.1	743.3	.27671
		147.1	.27614	25.1	748.8	.27671
		151.5	.27883	35.0	750.3	.27638
		164.7	.27906	34.4	751.4	.27672
		199.5	.27593	25.3	738.5	.27659
		238.5	.27572	25.1	738.9	.27646
		432	.27555	25.4	739.1	.27616
		453	.27391	21.4	739.4	.27633
		458	.27420	21.2	736.9	.27677
		479.5	.27543	25.0	735.3	.27627
						.27656 = Av.
Cell 88	.09066	12	.27920	25.2	739.1	.27990
		22	.27939	25.3	744.5	.27995
		37	.27890	25.2	742.3	.27954
		66	.27965	25.1	737.2	.27942
		85.4	.27830	24.9	727.9	.27931
		111.4	.27889	25.1	737.2	.27966
		135.4	.27915	25.2	743.3	.27977
		167.9	.28207	35.2	750.3	.27958
		180.9	.28203	34.4	751.4	.27969
		211.4	.27955	25.0	748.3	.28003
		216	.27913	25.2	738.4	.27984

Table III continued:

Cell 88	Conc.	Hrs.	E obs.	t obs.	Bar P. obs	E corr to 760 mm 25°C.
		255	.27880	25.1	738.9	.27954
		444	.27885	25.4	737.8	.27949
		464	.27772	21.4	739.4	.28014
		469	.27700	21.2	736.9	.27957
		492.5	.27872	25.1	735.3	.27952
						.27968 = Av.
Cell 89	.09066	14.3	.27909	25.3	739.1	.27974
		21	.27909	25.3	742.7	.27968
		46.4	.27907	25.2	742.3	.27971
		75.4	.27880	25.1	737.2	.27957
		92.1	.27860	24.9	728.2	.27961
		116.1	.27895	25.0	735.7	.27978
		144.1	.27929	25.2	743.3	.27991
		171.6	.27932	25.1	748.8	.27989
		193.6	.27947	25.1	749.3	.28003
		265.2	.27933	25.1	738.4	.28008
		454.6	.27945	25.1	739.4	.28018
		477.6	.28239	35.0	739.2	.28013
		481.1	.28221	34.9	736.9	.28001
						.27987 = Av.
Cell 90	.09066	13	.29014	25.2	742.3	.29078
		42	.28985	25.1	737.2	.29062
		60.4	.28960	24.9	728.2	.29061
		88.4	.28980	25.1	737.6	.29056
		112.9	.29048	25.2	742.5	.29112
		144.9	.29389	34.5	750.3	.29155
		157.5	.29382	34.4	751.2	.29149
		188.5	.29045	24.8	748.1	.29116
		192.9	.29040	25.2	738.4	.29111
						.29100 = Av.

Table IV shows the calculated temperature coefficients.

TABLE IV

Cell	$\frac{E_{av.}\ 34.4^\circ - E_{av.}\ 25.1^\circ}{9.3}$	$\frac{E_{av.}\ 25.1^\circ - E_{av.}\ 21.2^\circ}{3.9}$
86	.000347	.000447
88	.000355	.000473
89	.000340	-
90	.000424	-
	.000389 = Av.	.000460 = Av.

These average coefficients were plotted against the mean temperature changes and the curve (See Graph 2) used to obtain values for correcting the cells approximately 0.1M to 25° C. This included corrections for cells 22 to 93 inclusive.

Table III cell 86 shows clearly the effect of increase in temperature or the reverse effect of decrease in temperature.

For cells of concentration approximately 1.0 M, as the temperature increases there is a decrease in the e. m. f. of the cell. Cell No. 11_1 Table I is an example.

As the temperature decreases there is an increase in the e. m. f. See Table I cell No. 11_7.

The coefficients for temperature corrections of 1.0 M cells reported were obtained from study of temperature changes in cells No. 11_{1-8} Table I.

The calculated coefficients appear in Table V.

TABLE V

Cell	$\frac{\text{Eav. } 34.9^\circ - \text{Eav. } 25.1^\circ}{9.8}$	$\frac{\text{Eav. } 25.4^\circ - \text{Eav. } 21.2^\circ}{4.2}$
$11_{1,2,3,4}$	.0000714	———
$11_{5,7,8}$	———	.0000238

These average coefficients were plotted against the mean temperature changes (Graph 3) and the curve used to obtain values for correcting the cells approximately 1.0 M to 25°C. This included corrections for cells No. 1_{1-3} No. 11_{1-8} and No. 111_{1-6} inclusive. The correction values are of a much smaller order for more concentrated cells than for those cells of weaker concentration.

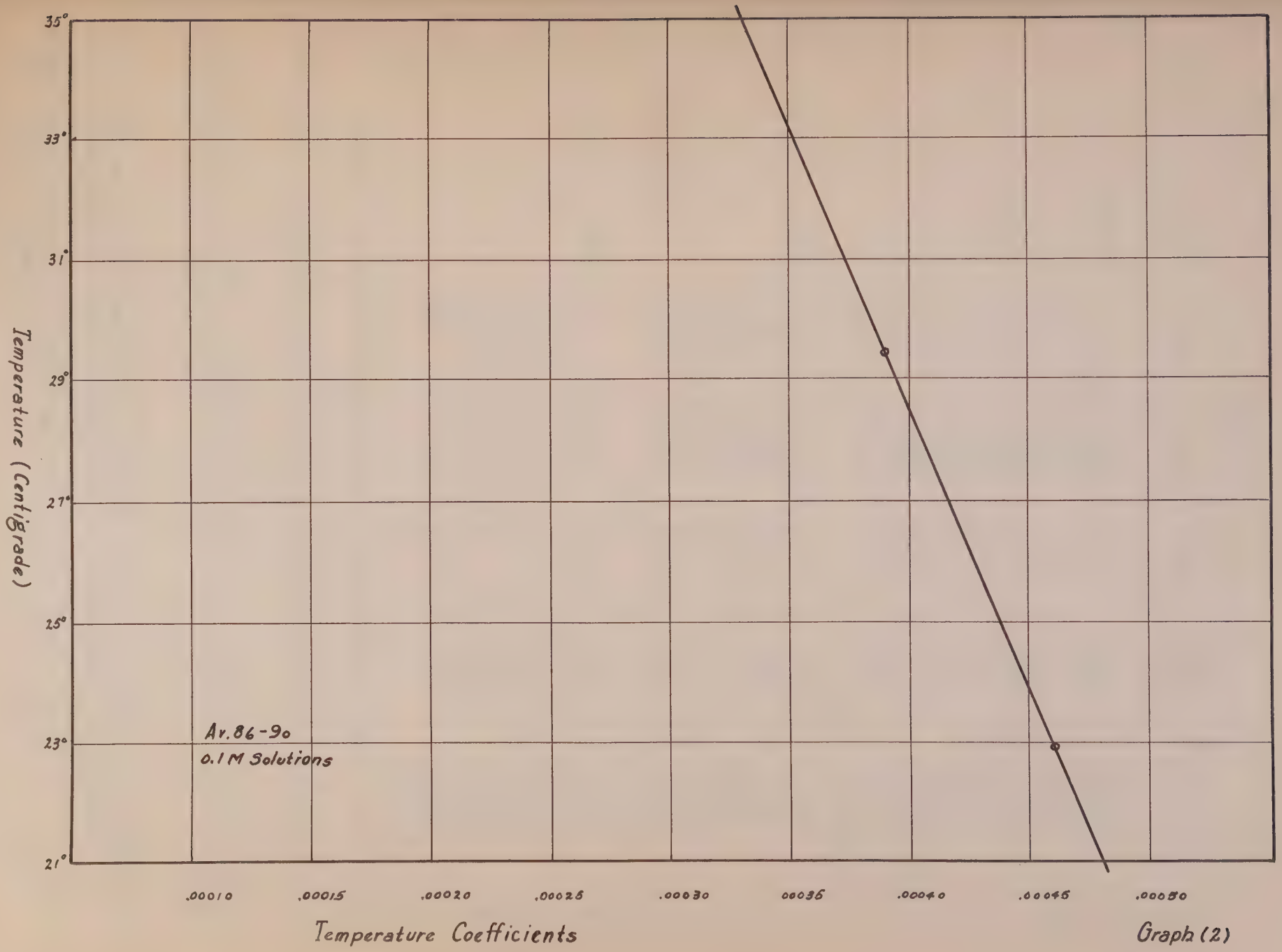
VII. CONSTANCY OF THE CELLS.

The cells containing more concentrated hydrobromic acid are much more constant than the cells containing weaker solutions. Table I exemplifies this fact. There are many variables which effect the constancy of the results of molal as well as tenth molal cells, but it is much more difficult to control these variables for weaker solutions.

Cell No. 22 was fairly constant for a period of over 295 hours. This cell was studied in the early part of the work and no attempt was made to measure it at 25°C. The temperatures given are those of room temperature for the cell was not placed in an oil bath.

Cell Nos. 30 and 35 are also good examples of how constant a cell may be even when tenth molal HBr was used. See Table VI for results.

Cells will be discussed later which show stability as well as other effects according to factors involved.


35°
33°
31°
29°
27°
25°
23°
21°
Temperature (Centigrade)
Av. 86-90
0.1 M Solutions
.00010
.00015
.00020
.00025
.00030
.00035
.00040
.00045
.00050
Temperature Coefficients

Graph (2)

TABLE VI

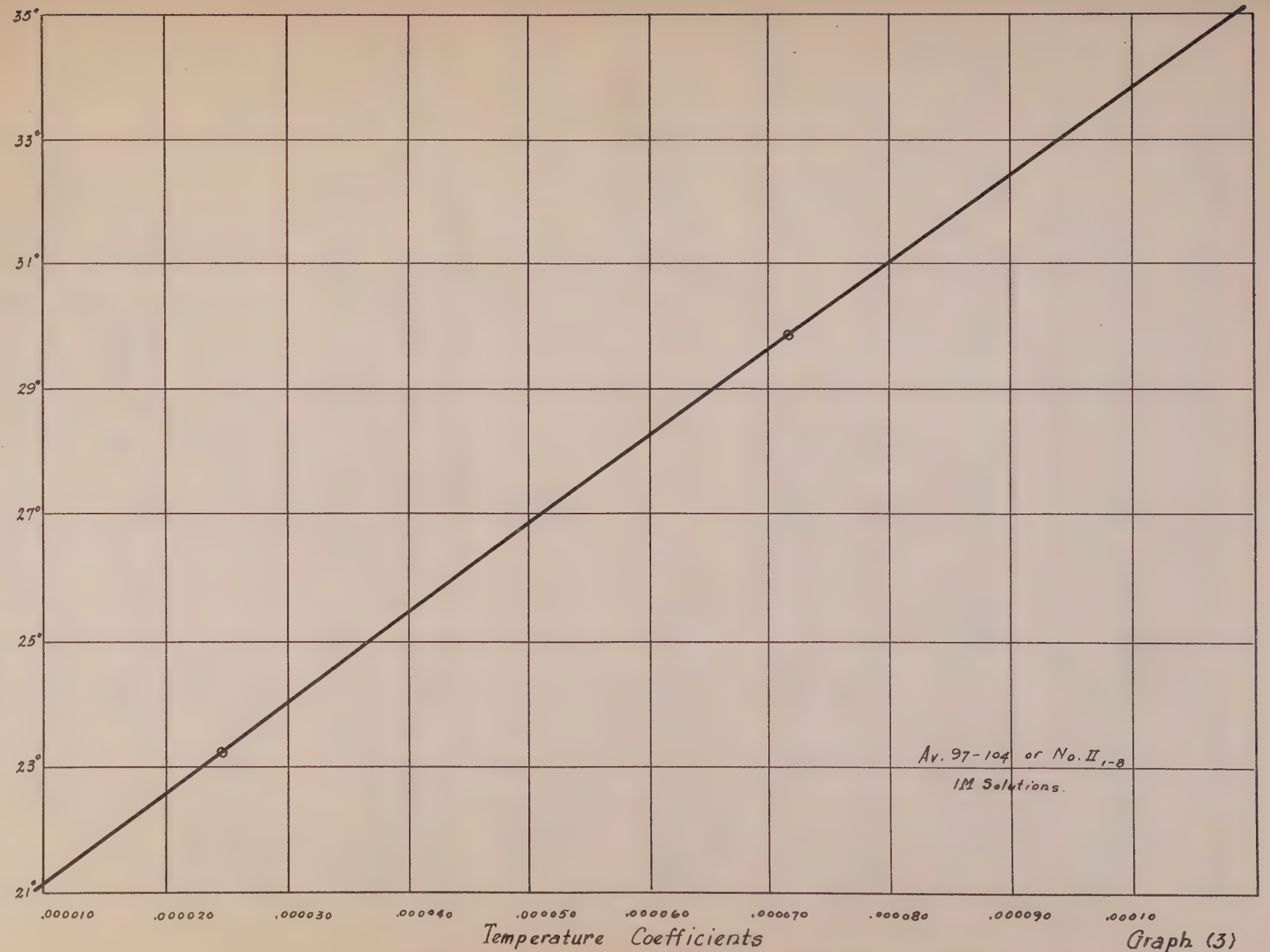
Cell 22	Conc.	Hrs.	E obs.	t obs.	Bar P. obs.	E corr to 760 mm 25°C.
	0.10015	1	.26826	24.2	745.2	.26928
		3.3	.26805	24.2	745.7	.26906
		10	.26808	24.4	746	.26899
		25	.26846	24.2	743	.26952
		32.6	.26766	24.2	737.8	.26881
		45.6	.26817	24	735.8	.26944
		56.6	.26826	24.1	739.9	.26941
		70.6	.26829	24	741.2	.26946
		77.6	.26828	24	735.5	.26955
		284.6	.26781	24.4	740.4	.26882
		289.6	.26777	24.2	730.6	.26887
		295.6	.26815	24.6	738.6	.26910
						.26919 = Av.
Cell 30	.0897	23.7	.27406	25	736.7	.27487
		44	.27408	24.9	740.6	.27488
		48.2	.27408	25	739.8	.27484
		66.6	.27394	24.6	743.4	.27481
		114.1	.27390	25	737.9	.27469
		159.7	.27373	25.1	736.2	.27451
		173.7	.27380	25	737.1	.27461
						.27474 = Av.
Cell 35	.10019	5	.27011	25	734.9	.27096
		18	.27011	25	737.9	.27090
		22.7	.27008	25	737.9	.27087
		41.5	.27008	25	738.6	.27086
		44.6	.27008	25	737.9	.27087
		47.6	.27015	25	737.8	.27095
		121	.27015	25.1	736.8	.27092
		143	.27015	25	736.6	.27097
						.27091 = Av.

VIII. EFFECT OF CONCENTRATION CHANGE ON THE ELECTROMOTIVE FORCE OF THE CELL

If the concentration of the electrolyte is approximately 0.1 M the e. m. f. of the cell is decreased with increased concentration on each half cell.

When Cell No. 79 (See Table VIII) was 242 hours old and still stable, 2 c.c. of constant boiling HBr were put in the H-half cell. In 5 hours a measurement was made showing a decrease of 0.00630 volt. Two hours later there was an additional decrease of 0.01330 V.

Cell 75 of concentration 0.11053 M was used in the study of this effect. This cell was fairly constant and at the end of 119 hours, 2 c.c. of constant boiling HBr were put into the mercurous bromide electrode. In 3 hours a measurement showed a decrease of 0.13045 V. At this time, 2 c.c. of constant boiling HBr were added to the H-half cell. After 1 hour the e. m. f. had further decreased 0.01688 V.


35°
33°
31°
29°
27°
25°
23°
21°
Temperature (Centigrade)
.000010
.000020
.000030
.000040
.000050
.000060
.000070
.000080
.000090
.00010
Temperature Coefficients
Av. 97-104 or No. II, 1-8
1M Solutions.

Graph (3)

The effect of increase in the concentration of the electrolyte is much more rapid in the H-half cell than in the Hg_2Br_2 half cell.

Several cells were studied to determine the effect of a decrease in concentration. One c.c. of water was added to the hydrogen electrode of cell 72 (C = 0.11053 M) which had stayed constant for a period of 138 hours. In 40 minutes there was a decrease in the e. m. f. of 0.03874 volt. Thirty-five minutes later there was a further decrease of 0.03520 volt.

Cell 80 (C = 0.09785 M) constant for 204 hours was treated in a similar manner. In 20 minutes there was a decrease of 0.02600 V. Water was then added to the Hg_2Br_2 half cell and measured. The drop in e. m. f. in the same length of time was 0.00700 V. This retarded effect in decrease was noted and the results checked by use of another cell.

Cell 83 (C = 0.09785 M) was stable 159 hours. To this water was added first to the Hg_2Br_2 half cell, showing an increase of 0.00185 V in 15 minutes.

Cell 87 (C = 0.09066 M) (See Table VIII) constant for 141 hours was treated in a manner similar to the preceding cell. In the same length of time there was an increase of 0.00104 V in e. m. f.

Cell 88 (C = 0.09066 M) (See Table III) was treated with water which had been saturated with H_2 gas. The water was added to the H-half cell when it was 504 hours old. Thirteen and a half hours later a measurement showed a decrease of 0.01163 V. Water was then added to the Hg_2Br_2 half cell and 4 hours afterwards there was an additional decrease of 0.01248 V.

Decreasing the concentration of a complete cell of the above types shows an increase in e. m. f. In this the HBr cell is similar to the HCl cell. This is shown in the difference in values for e. m. f. between 0.1 M and 1.0 M cells. (See 86 C = 0.09066 M Table III) and No. 11_1 (C = 0.9745 M Table I.)

For cells approximately 1.0 M the same effects were studied. The reverse of the above results was noted. Adding water to the H-half cell causes an increase in e. m. f., while addition of water to the Hg_2Br_2 electrode causes a decrease in e. m. f. The increase in the case of the H-half cell is large in comparison to the decrease noted in the case of the Hg_2Br_2 electrode. In Table VII will be seen continuation of Cell No. 11_5 and Cell No. 11_7 from Table I showing effect of change in concentration on the e. m. f.

TABLE VII

Cell No. 11_5	Hrs.	E obs.	t obs.	Bar P. obs.	E corr. to 760 mm 25°C.	Conc.
	240.1	.14709	25	733.3	.14788	.9745
	Water saturated with H_2 gas added to the H-half cell					
	295.1	.14726	25	733.3	.14805	
	298.6	.14728	25.1	731	.14812	
Cell No. 11_7	238.5	.14708	25	733.3	.14787	
	Water added to the Hg_2Br_2 electrode					
	257.5	.14703	25	733.4	.14782	

Table VII continued:

Cell No. 11_7	Hrs.	E obs.	t obs.	Bar P. obs.	E corr. to 760 mm 25°C.	Conc.
	Water added to the H - electrode					
	258.5	.14767	25.1	733.4	.14847	
	261.5	.14765	25.0	731	.14848	

For comparison of increase in concentration see Cell No. 11_7 Table I and No. 86 Table III.

IX. THE EFFECT OF AGITATION.

The stability of the cells depends upon a large number of variables, the most important of which is that of the equilibrium of the HBr solution with suspended Hg_2Br_2. The difficulties met when working with weaker concentrations seem to be such as to bring up the question of whether or not the value of the cell does not depend almost wholly on the period of time the solution is shaken.

With this in mind two series of experiments were carried out, in which the HBr solution was shaken mechanically with Hg_2Br_2 for varying lengths of time, ranging from 45 minutes to as high as 96 hours. The results are presented in Table VIII, Table IX, and in Graph (4). It is noticeable that a maximum appears for the value near the 12 hour shaking period.

TABLE VIII

Cell 77	Hrs.	E obs.	t obs.	Bar P. obs.	E corr. to 760 mm 25°C.	Conc.
	40.5	.26925	24.76	739.2	.27013	.09785
	58.5	.26871	24.72	737.8	.26963	
	76	.26846	24.68	740	.26936	
	101	.26864	24.70	748.7	.26938	
	126.4	.26800	24.68	748.9	.26875	
	173.3	.26838	24.72	736	.26933	
	189.3	.26750	24.70	737	.26844	
	213.3	.26790	24.70	738.5	.26882	
					.26923 = Av.	
Cell 78	15.3	.26983	24.73	739.5	.27071	.09785
	40.7	.26863	24.76	739.2	.26951	
	58.7	.26495	24.72	737.8	.26587	
	75.7	.24527	24.68	740	.24617	
	104.7	.26593	24.7	748.3	.26668	
	123.7	.26367	24.66	748.9	.26443	
					.26389 = Av.	
Cell 79	23	.26857	24.74	738.6	.26946	.09785
	40	.26838	24.76	739.4	.26925	
	65.7	.26821	24.7	739.8	.26910	
	88.7	.26874	24.68	740	.26964	
	112.7	.26862	24.7	748.3	.26937	

Table VIII continued:

Cell 79	Hrs.	E obs.	t obs.	Bar P. obs.	E corr. to 760 mm 25°C.	Conc.
	155	.26858	24.68	748.9	.26933	
	176	.26873	24.72	732	.26975	
	198.5	.26864	24.7	737.3	.26958	
	223	.26842	24.72	738.5	.26933	
	242	.26835	24.72	740.8	.26922	
					.26940 = Av.	
Cell 80	23	.26847	23.2	738.6	.27005	.09785
	39	.26847	23.2	738.6	.27053	
	64.6	.26806	23.4	739.8	.26952	
	87.6	.26803	24.4	740	.26915	
	115.6	.26947	25.2	748.3	.27001	
	133.1	.26959	25.2	748.9	.27012	
	189.1	.26920	25	731.6	.27010	
	204.1	.26870	25.1	740	.26942	
					.26986 = Av.	
Cell 81	18	.27091	25	739.4	.27168	.09785
	40	.26997	23.8	741.5	.27122	
	66.7	.27018	23.6	740.7	.27153	
	110.7	.27104	25.2	748.9	.27157	
	159.5	.27058	25	736.1	.27140	
	185.7	.27083	25	737.3	.27163	
	211.7	.27086	25.05	738.5	.27162	
	228.2	.27083	25.1	740.8	.27154	
	258.2	.27029	24.72	736.4	.27123	
					.27149 = Av.	
Cell 82	18	.27096	25	739	.27174	.09785
	40	.27012	23.8	741.5	.27137	
	66.7	.26931	23.6	740.7	.27066	
	86.7	.26924	22.1	748.7	.27117	
	151.2	.26964	25	732	.27053	
	176.4	.27084	25.1	737	.27161	
	201.4	.27077	25.05	738.5	.27153	
	221.4	.27087	25.1	740.2	.27159	
					.27126 = Av.	
Cell 83	23.8	.27065	24.3	743.4	.27165	.09785
	51.8	.27095	23.9	740.7	.27217	
	74.3	.27097	23	748.3	.27247	
	78.3	.27056	25.2	748.3	.27100	
	95.9	.27054	25.2	748.9	.27107	
	136.9	.27123	25	732	.27212	
	159.9	.27138	25.1	738.5	.27213	
	180.4	.27135	25.1	740.8	.27206	
					.27183 = Av.	
Cell 84	23.8	.27074	24.3	743.4	.27174	.09785
	51.8	.27016	23.9	740.7	.27138	
	76.3	.27090	25.1	748.3	.27148	
	96.8	.27086	25.2	748.9	.27139	
	151.8	.27083	25	731.6	.27173	
					.27154 = Av.	

Table VIII continued:

Cell 86	Hrs.	Obs. E	t obs.	Bar P. obs.	E corr to 760 mm 25°C.	Conc.
	46.4	.27621	25.2	742.3	.27685	.09066
	64.4	.27580	25.1	737.2	.27657	
	83.4	.27559	24.9	727.5	.27661	
	98.9	.27597	25.1	737.6	.27673	
	116.9	.27605	25.1	743.3	.27671	
	147.1	.27614	25.1	748.8	.27671	
	151.5	.27883	35	750.3	.27638	
	164.7	.27906	34.4	751.4	.27672	
	199.5	.27593	25.3	738.5	.27659	
	238.5	.27572	25.1	738.9	.27646	
	432	.27555	25.4	739.1	.27616	
	453	.27391	21.4	739.4	.27633	
	458	.27420	21.2	736.9	.27677	
	479.5	.27543	25	735.3	.27627	
					.27656 = Av.	
Cell 87	6.6	.27720	25.2	734.9	.27797	.09066
	22.6	.27703	25.3	740.9	.27765	
	29.9	.27731	25.3	744.5	.27787	
	45.4	.27673	25.2	742.3	.27737	
	74.9	.27653	25.1	737.2	.27730	
	94.9	.27605	24.9	727.5	.27707	
	120.5	.27629	25.1	737.6	.27705	
	140.9	.27636	25.1	743.4	.27702	
					.27741 = Av.	
Cell 88	12	.27920	25.2	739.1	.27990	.09066
	22	.27939	25.3	744.5	.27995	
	37	.27890	25.2	742.3	.27954	
	66	.27865	25.1	737.2	.27942	
	85.4	.27830	24.9	727.9	.27931	
	111.4	.27889	25.1	737.2	.27966	
	135.4	.27915	25.2	743.3	.27977	
	167.9	.28207	35.2	750.3	.27958	
	180.9	.28203	34.4	751.4	.27969	
	211.4	.27955	25	748.3	.28003	
	216	.27913	25.2	738.4	.27984	
	255	.27880	25.1	738.9	.27954	
	444	.27885	25.4	737.8	.27949	
	464	.27772	21.4	739.4	.28014	
	469	.27700	21.2	736.9	.27957	
	492.5	.27872	25.1	735.3	.27952	
					.27968 = Av.	
Cell 89	14.3	.27909	25.3	739.1	.27968	.09066
	21	.27909	25.3	742.7	.27968	
	46.4	.27907	25.2	742.3	.27971	
	75.4	.27880	25.1	737.2	.27957	
	92.1	.27860	24.9	728.2	.27961	
	116.1	.27895	25	735.7	.27978	
	144.1	.27929	25.2	743.3	.27991	
	171.6	.27932	25.1	748.8	.27989	

Table VIII continued:

Cell 89	Hrs.	Obs. E	t obs.	Bar P. obs.	E corr. to 760 mm 25°C.	Conc.
	193.6	.27947	25.1	749.3	.28003	
	265.2	.27933	25.1	738.4	.28008	
	454.6	.27945	25.1	739.4	.28018	
	477.6	.28239	35	739.2	.28013	
	481.1	.28221	34.9	736.9	.28001	
					.27987 = Av.	
Cell 90	13	.29014	25.2	742.3	.29078	.09066
	42	.28985	25.1	737.2	.29062	
	60.4	.28960	24.9	728.2	.29061	
	88.4	.28980	25.1	737.6	.29056	
	112.9	.29048	25.2	742.5	.29112	
	144.9	.29389	34.5	750.3	.29155	
	157.5	.29382	34.4	751.2	.29149	
	188.5	.29045	24.8	748.1	.29116	
	192.9	.29040	25.2	738.4	.29111	
					.29100 = Av.	
Cell 91	25.5	.28991	25.2	742.3	.29055	.09066
	42.9	.28978	25.1	737.2	.29055	
	61.3	.28984	24.9	727.9	.29085	
	86.8	.28971	25.1	737.6	.29047	
	110.8	.29092	25.2	743.3	.29154	
	141.4	.29120	25.1	748	.29172	
	207.4	.29124	25.1	737.1	.29201	
					.29109 = Av.	
Cell 92	3	.28538	22.6	727.5	.28742	.09066
	23	.28587	23	735.7	.28759	
	76	.28629	21.4	748	.28856	
	99	.28716	25	749.3	.28776	
	146	.28703	25.1	737.1	.28780	
					.28782 = Av.	
Cell 93	3	.28776	22.6	727.5	.28980	.09066
	22.6	.28785	23	735.7	.28957	
	73.1	.28624	21	748	.28873	
	99.1	.28692	25.1	749.3	.28748	
					.28889 = Av.	

TABLE IX

	Cell	Conc.	Time Shaken	Average of E corr. to 760 mm 25°C.	Average of Duplicate cells	Series II corr. to .09785 M	
Series I	77	.09785M	.75Hrs.	.26923	.26923		
	78	"	.75 "	(26390)			
	79	"	4 "	.26940			
	80	"	4	.26986	.26963		
	81	"	21.5 "	.27149	.27138		
	82	"	21.5 "	.27126			
	83	"	47 "	.27183	.27169		
	84	"	47 "	.27154			
				.27066 = Av.			
							Av.
Series II	86	.09066M	4Hrs.	.27656	.27699	.26318)	.26361
	87	"	4 "	.27741		.26403)	
	88	"	12 "	.27968	.27978	.26630)	.26640
	89	"	12 "	.27987		.26649)	
	90	"	36 "	.29100	.29105	.27762)	.27767
	91	"	36 "	.29110		.27772)	
	92	"	96 "	.28783	.28837	.27445)	.27499
	93	"	96 "	.28890		.27552)	
				.28404 = Av.			

.28404 = Av. E of Series II
.27066 = " " " " I
.01338 = Δ E

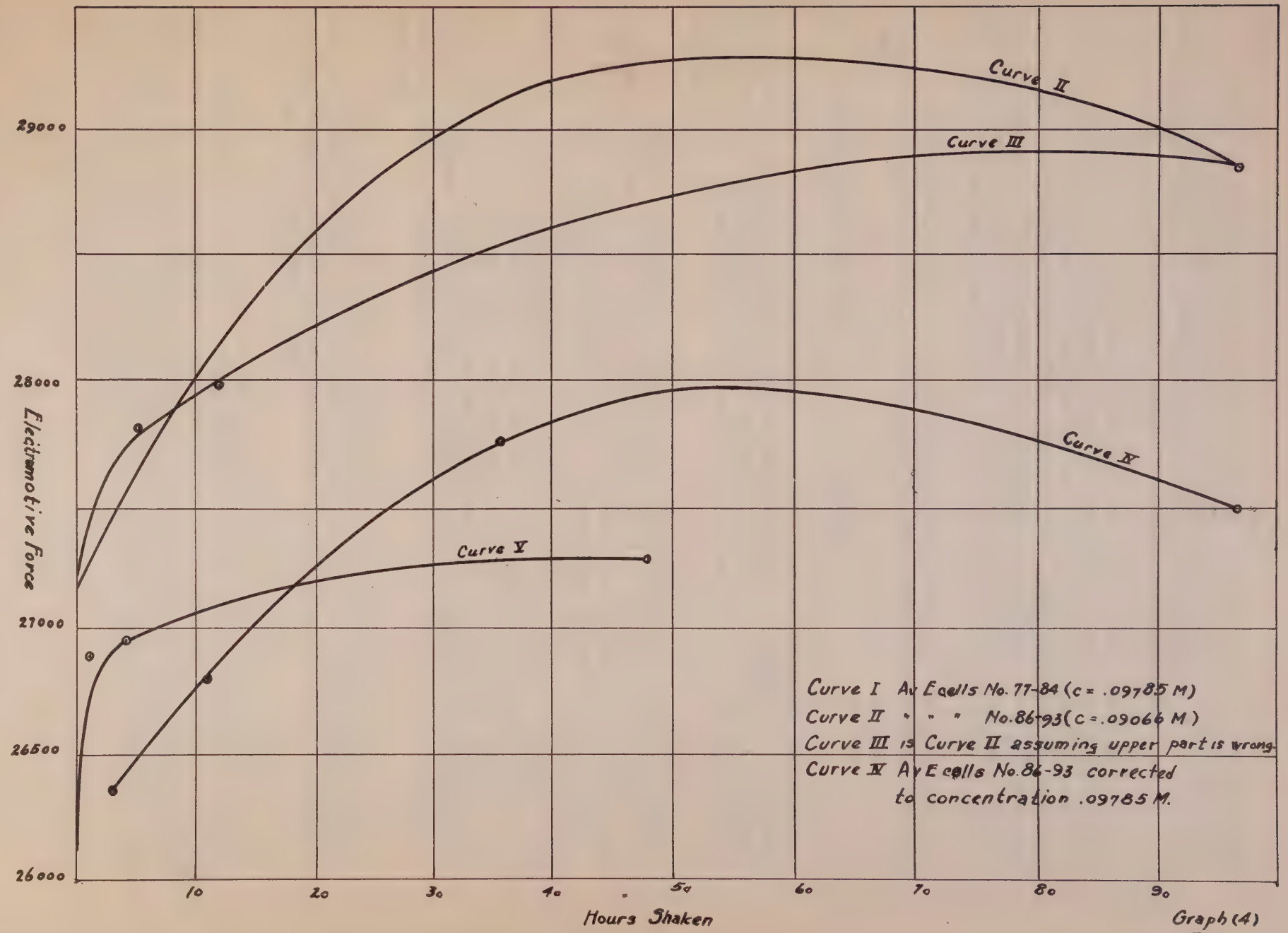
.09785M = Conc. of Series I
.09066M = " " " II
.00719M = Δ Conc.

.001M $\approx$ .00186

It had been noted that cells shaken by hand sometimes gave nearly as good results as those shaken mechanically for somewhat varying periods of time. Cells shaken for as short a period as 45 minutes did not reach equilibrium while those shaken for 96 hours gave values which were quite low but rather stable.

Several explanations for this apparent anomaly seem worthy of consideration. Undoubtedly the solutions shaken for shorter periods of time had not reached adsorption equilibrium. It is well known that precipitates of fine particles are more soluble than those of large particles and that the adsorptive capacity of the fine particles is greater than that for larger particles. It therefore seems plausible that as time for agitation increases, the finer particles dissolve and thus affect the concentration of the solution in a two fold manner.

The substance adsorbed is set free and the concentration of the solution is increased. This is evidenced by a lowering of the e. m. f. of the cell. In the second place the adsorptive capacity of the precipitate is lowered because the surface is greatly diminished due to formation of large particles at the expense of the smaller ones and thereby decreasing greatly the interface surface.


Curve II
Curve III
Curve IV
Curve V
29000
28000
27000
26500
26000
Electromotive Force
10
20
30
40
50
60
70
80
90
Hours Shaken
Curve I Av E cells No. 77-84 (c = .09785 M)
Curve II " " " No. 86-93 (c = .09066 M)
Curve III is Curve II assuming upper part is wrong.
Curve IV Av E cells No. 86-93 corrected
to concentration .09785 M.

Graph (4)

The rate of adsorption is greater than the rate of solubility of fine crystals. In higher concentrations the rate of adsorption is greater but the per cent change in concentration is less. Therefore the per cent change in e. m. f. is not so apparent when the concentration is large.

If active HBr is removed from solution due to adsorption by Hg_2Br_2, the active HBr present is less when more fine particles are in suspension than coarse ones, on account of the greater surface offered. This is shown to be true from the results given. The curves on the graph show how the E gradually increases with a decrease in concentration and then as the finer particles dissolve with increased agitation, the E decreases, due to an increase in concentration which would occur as the adsorbed substance was set free.

In an article by W. A. Patrick (J. Phys. Chem. 30, 134 (1926) it is intimated that the e. m. f. of cells may be affected by the adsorption of ions.

X. EFFECT OF LIGHT ON THE E. M. F. OF THE CELL

It has been shown experimentally that light is adsorbed by hydrogen halides and that the potential of mercury covered with Hg_2Br_2 is influenced by adsorption of light. All precautions were taken to protect the HBr and Hg_2Br_2, while being prepared or used, from this effect. Gerke also guarded against this effect.

Series of experiments were carried out to study the effect of illumination on the e. m. f. of the cell. Cell 84 (C = .09785M) Table VIII, when 169 hours old was used. First the H-half cell was exposed to a 100 W. light at a distance of 6 inches for 2 hours. It was then returned to the dark room and after an hour the e. m. f. had decreased .00006 V. Then the Hg_2Br_2 half cell was treated in the same manner for the same length of time. When equilibrium was reestablished and the e. m. f. measured, it was found to have increased .00006 V. and this was persistent. This effect was contrary to expectation in that the value seemed to change and then tended to remit to the equilibrium value. No visible change seemed to be apparent, but there may have been an appreciable effect during the time the cell was actually exposed.

Measurements were made on cells with and without exposure to light and the results showed that the effect is uncertain and that reversibility is like that of a high velocity reaction. (See A. Berthoud and G. Nicolet - Helv. Chim. Acta 10, 475 (1927).

The effect of light was studied when the electrolyte of the cell was approximately 1.0 M. Cell No. 113 (Table I) after being constant 239 hours was used in the experiment. The H-half cell was exposed 12 hours to a 100 W. light in the manner described above. It was then put back in the thermostat and when equilibrium had been reestablished the e. m. f. showed a decrease of 0.00020 V. After 141.8 hours there was an additional decrease of 0.00007 V. showing a tendency toward a gradual decrease in e. m. f.

Cell No. 11_4 of the same concentration as the previous cell (Table I), constant for 239.7 hours, was used to study the effect of illumination on the Hg_2Br_2 half cell. The exposure was again for 12 hours. When equilibrium had been reached, the e. m. f. measurement showed a decrease of 0.00056 V. Five hours later there was an additional loss of 0.00030 V, but at the end of 44 hours an increase of 0.00013 V. was apparent.

For cells of both 0.1 M and 1.0 M solutions, illumination of the H-half cell causes a persistent decrease in e. m. f., while illumination of the mercurous bromide electrode causes a decrease at first and then a gradual increase after a period of time. So with cells of lower concentration of HBr the change is in the same direction as for higher concentrations but the degree of change was much less. In fact it is uncertain if the change is positive or negative.

A similar effect for AgBr has been noted by Sheppard (J. Phys. Chem. 33, 331 (1929) and is believed to be the same for Hg_2Br_2 but of a much smaller order. The velocity of the change is too high and undoubtedly too great to be measured by the Type K or Wolff potentiometers. The fact that the change is reversible is noteworthy in view of the different theories relative to the nature of the change. This phenomenon is of the same order as that produced by increasing the temperature of cells with concentration 0.1 M or 1.0 M.

In general one may assume that the effects are not of a chemical nature and furthermore are quite reversible and are not permanent in that no permanent effect on the e. m. f. is produced.

XI. EFFECT OF BROMINE IN THE CELL.

When Br_2 is present in the H-half cell, there is a strong tendency for the e. m. f. to decrease. If there is enough Br_2 present there will be a rapid reversal of polarity. But the effect gradually disappears and the cell becomes fairly constant again. Br_2 in the Hg_2Br_2 half cell has little permanent effect, but if the mercuric salt were formed, the e. m. f. measurements become erratic.

Cell No. 86 (Table VIII) after being fairly constant for 482 hours, was treated with Br_2 which had been dissolved in acid of the same concentration as the cell electrolyte. This was added to both half cells and 19.5 hours later a measurement showed a very slight change. Then Br_2 treated in the same manner was added to the H-half cell. Ten minutes later Br_2 was added to the Hg_2Br_2 half cell. The results are given in the following table:

TABLE X

Hrs.	E obs.	E corr. to 760 mm. 25°C.
479.5	.27543	.27627
482.	.27541	.27628
501.5	.27548	.27631
5 Min. later	.27490	.27573
3 " "	.27491	.27574
2 " "	.27504	.27587
10 " "	.27531	.27614
20 " "	.27538	.27621
1½ Hrs.	.27541	.27628

Several Hg_2Br_2 half cells with 0.1 M electrolyte were made up in H-tubes and their constancy as well as the effect of addition of Br_2 noted.

TABLE XI

Hrs.	E obs.	Hrs.	E obs.
1	.00003	264.9	.00016
25.5	.00010	3168.9	.00005
70.5	.00030	3184.9	.00003
116.5	.00031		
164.5	.00026		
212.5	.00019		

After this period of time Br_2 vapor was poured into the positive arm of the H-tube. The e. m. f. increased to about 0.00030 V. immediately.

Hrs.	Obs. E
3211.9	.00007
3307.4	-.00007
3329.4	.00005

Br_2 vapor was again poured into the positive arm and in 45 minutes the e. m. f. had increased to 0.00071 V. Three hours later the e. m. f. was 0.00110 V, but after 7 days it had decreased to 0.00010.

This same effect was studied in a complete cell where the electrolyte was 0.9745 M. The results were similar, but the bromine effect takes a much longer period of time to disappear than in the case of 0.1 M cells. The effect of Br_2 on the Hg_2Br_2 electrode is much more marked for this higher concentration. Cell No. 11_1 (Table I) had been very stable over a period of 240.3 hours. At this time Br_2, dissolved in acid of the same concentration as in the cell, was added to the H-half cell. The following table shows the results clearly.

TABLE XII

Hrs.	E obs.	E corr. to 760 mm. 25°C.
240.3	.14768	.14847
260.3	.14703	.14782
264.7	.14715	.14798
266.7	.14740	.14822
284.3	.14741	.14819
383.7	.14768	.14823

Cell No. 11_2 (Table I) had been stable for 241.6 Hrs. when the Hg_2Br_2 half cell was treated with Br_2 in a similar manner. Table XIII shows the result:

TABLE XIII

Hrs.	E obs.	E corr. to 760 mm. 25°C.
241.6	.14748	.14827
260.6	.14731	.14810
265.6	.14719	.14802
266.1	.14719	.14802
285.5	.14715	.14792

XII. THE EFFECT OF THE PRESENCE OF OXYGEN IN THE CELL.

Two cells were made to study the effect of oxygen in the Hg_2Br_2 solution in the e. m. f. The two cells were identical with the exception that in the second cell, the Hg_2Br_2 solution was saturated with oxygen before it was rotated.

TABLE XIV

Cell 31	Hrs.	E obs.	t obs.	Bar P. obs.	E corr. to 760 mm. 25°C.
	29.2	.26844	25.8	738.4	.26890
	43.2	.26844	24.98	739.7	.26920
	67.8	.26831	25	742.6	.26902
	69.2	.26831	25.18	742.4	.26896
	71.1	.26835	25.3	741.9	.26895
	72.1	.26835	25.3	741.9	.26895
Cell 32	26.5	.27100	27.2	738.2	.27092
	27.3	.27350	27.0	738.2	.27351
	43.5	.27446	25.02	739.2	.27523
	44.3	.27513	25.11	738.6	.27587
	64.8	.27568	25.12	742.6	.27642
	71.7	.27592	25.31	741.9	.27652
	72.6	.27610	25.18	741.9	.27676

Oxygen present in the Hg_2Br_2 half cell causes an increase in the e. m. f. of the cell.

The effect of oxygen in the H-half cell was studied and conclusions drawn from the following results.

TABLE XV

Cell 68	Hrs.	E. obs.	t obs.	Bar P. obs.	E corr. to 760 mm. 25°C.
	27	.26733	24.77	742.3	.26815
	29	.26733	24.82	742.1	.26813
	58	.26764	25.18	737.5	.26837
	73	.26721	24.76	733.7	.26818
	98	.26724	24.78	740.7	.26808
	126	.26590	24.8	742.5	.26670
	199.4	.26570	24.8	728	.26675

At the end of 199.4 hours oxygen was run through the H-half cell. There was a numerical decrease in the e. m. f. of .65948 V. Forty-eight hours later H_2 gas was passed into the cell for 3 hours and a measurement showed the e. m. f. to be within 3 mv. of the value recorded before oxygen was admitted.

Oxygen in the Hg_2Br_2 half cell caused too high a value for the e. m. f., while O_2 in the H-half cell causes a rapid decrease in the e. m. f. with change in polarity. This second effect can be reversed unless oxidation has occurred in the cell constituents.

This work was done under the direction of Dr. Dwight T. Ewing at the Kedzie Chemical Laboratory.

XIII. SUMMARY.

1. The potential between colloidal mercurous bromide and a solution of hydrobromic acid varies considerably with the method for preparing the mercurous bromide. In this connection the value of the electromotive force and the stability of the system mercury and mercurous bromide, hydrobromic acid (m), hydrogen and platinum has been investigated. Very accurate results have been obtained and there appears to be a direct relationship between the activity of the colloidal bromide and the equilibrium value of the e. m. f. of a cell for this system.

Heretofore this system has not been investigated except by Gerke and Geddes who made measurements for only a concentration of a tenth formal hydrobromic acid in a cell which would permit of some diffusion, a defect which has been overcome in this work by a cell of a new design.

2. From the values of the e. m. f. of cells of the type H_2 (g), HBr (M), Hg_2Br_2 (s), Hg (l) and the activity coefficient for HBr, (0.868, Harned), it is shown that the single electrode potential of the half cell Hg (l), Hg_2Br_2 (s), Br^- is 0.1396 V.

3. The value of the e. m. f. of the cells of the lower concentrations was shown to vary with time of shaking, passing through a maximum and later diminishing to constant value.

4. For cells of tenth molal concentration as the temperature increases, the e. m. f. increases and as temperature decreases the e. m. f. decreases. The reverse is true in the case of cells of molal concentration.

5. Cells of 0.1 M concentration as well as 1 M are stable in the absence of oxygen and light.

6. As concentration of 0.1 M cells increases the e. m. f. decreases. The reverse is true in the case of 1 M cells. The effects of change in concentration of either half cell was noted.

7. The Hg_2Br_2 electrode is influenced by absorption of light, but the effects produced are not chemical and are reversible.

8. Bromine does not effect the E permanently.

9. Presence of oxygen causes an increase in the E.